Phytochemistry, Vol. 28, No. 2, pp. 599–605, 1989.
Printed in Great Britain.

0031–9422/89 $3.00 + 0.00

TWO PYRANODIHYDROBENZOXANTHONES FROM *ARTOCARPUS NOBILIS*

M. UVAIS S. SULTANBAWA and SIVAGNANASUNDRAM SURENDRAKUMAR*

Department of Chemistry, University of Peradeniya, Sri Lanka

(*Received* 7 *April* 1988)

Key Word Index—*Artocarpus nobilis*; Moraceae; bark; dihydrobenzoxanthones; biosynthesis; artobiloxanthone; cycloartobiloxanthone.

Abstract—Two new pyranodihydrobenzoxanthones have been isolated from the bark of *Artocarpus nobilis* and their structures established as 5,6,11-trihydro-1,3,4,8-tetrahydroxy-5-isopropenyl-11,11-dimethylbenzo[1,2:*a*]pyrano [2′,3′:*j*]xanthene-7-one (artobiloxanthone) and 5,5a, 6,11-tetrahydro-1, 3, 8-trihydroxy-5, 5, 11, 11-tetramethylbenzofuro [3,3*a*,4:*ab*] pyrano [2′,3′:*j*]xanthen-7-one (cycloartobiloxanthone). This is the first report of the occurrence of dihydrobenzoxanthones in plants. A plausible biosynthetic route is proposed for the benzoxanthones from a simple flavone.

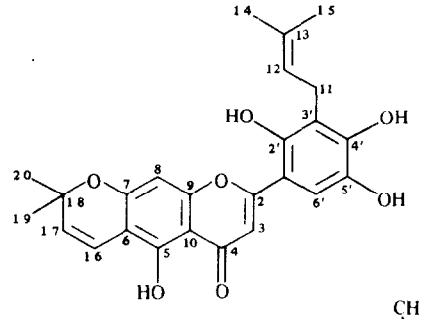
INTRODUCTION

Artocarpus nobilis is the only endemic species of the genus *Artocarpus* belonging to the family Moraceae found in Sri Lanka. Earlier investigations of the species yielded several chromenoflavonoids [1]. In the present study three yellow pigments were isolated from the bark of *A. nobilis*, two of which were shown to contain a dihydrobenzoxanthone moiety, the third compound artobilochromen (**1**) being a flavone found previously [1]. Although several prenylated flavonoids are known [2], so far as we are aware, there is only one report [3] of the isolation of a benzoxanthone glucoside, dillanoside (**2**) from the fruits of *Anethum graveolens* L. (Umbelliferae). This is the first reported occurrence of dihydrobenzoxanthones in plants.

RESULTS AND DISCUSSION

The most polar compound of the three, artobiloxanthone (**3a**), mp 162–164°, on high resolution mass spectrometry revealed a $[M]^+$ *m/z* 434.1306 and analysed for the molecular formula $C_{25}H_{22}O_7$. The compound gave a bright yellow trimethyl ether (**3b**), $[M]^+$ *m/z* 476.1837 ($C_{28}H_{28}O_7$) with diazomethane which showed a downfield signal (δ13.30) for a chelated hydroxy group in the ^{1}H NMR spectrum, while acetylation with acetic anhydride–pyridine yielded a tetra-acetate (**3c**) $[M]^+$ *m/z* 602.1813 ($C_{33}H_{30}O_{11}$). The IR spectrum showed hydroxyl and xanthone carbonyl absorptions at 3300 and 1650 cm^{-1}, respectively [4]. Colour tests with iron (III) chloride (green) and magnesium–conc HCl (orange), together with the characteristic UV spectral data indicated that the compound possesses a xanthonoid chromophore [4]. The presence of an *ortho*-dihydroxy system was revealed by the bathochromic shift ($\Delta\lambda$15 nm) in the UV spectrum with NaOAc–H_3BO_3 [5]. The pyranoxanthonoid structure was confirmed by the ^{1}H NMR spectrum in acetone-d_6. The superimposed singlets for the two chromen methyl groups at δ1.40, together with the two doublets (J = 10 Hz), each due to olefinic protons at δ6.92 and 5.64, are characteristic of a 2,2-dimethyl chromene. This was supported by the base peak obtained in the mass spectrum of artobiloxanthone (**3a**) at *m/z* 419 $[M-Me]^+$ [6]. A singlet was observed for the allylic methyl group at δ1.74 and two multiplets at δ4.60 and 4.30 for the methylene protons suggesting the presence of an isopropenyl group in the compound. The dihydro nature of the benzoxanthone was clearly shown by an ABX system at δ3.94 (*d*,H, J = 8 Hz), 3.41 (*dd*, J = 2 and 16 Hz) and 2.37 (*dd*, J = 8 and 16 Hz). This must have arisen by the oxidative cyclization of the isoprenyl unit with the highly nucleophilic B-ring, similar to that proposed for the neoflavonolignan, neohydnocarpin (**5**), where a luteolin moiety and a coniferyl alcohol moiety are linked by a C–C bond. [7]. This was supported by the presence of methine (δ_c38.2) and methylene (δ_c22.3) carbon atoms in the ^{13}C NMR spectrum of **3a** (see Table 1). Aromatic protons in **3a** appeared as two singlets at δ6.57 and 6.10, the latter arising from H-6 as in 6-deoxyisojacareubin (**6**) which also possesses a dimethyl pyran ring and a hydrogen bonded hydroxy group [8]. The high value of the other proton (H-3′) is attributed to the effect of the electron donating substituents in the B-ring [9]. The paramagnetic shifts [10] of the chromen ring protons in the trimethyl ether (**3b**) and tetra-acetate (**3c**) and the negative Gibbs test [11] given by **3a** are in agreement with the angular orientation of the dimethyl pyran ring (Table 2). As the Gibbs test can be capricious [12], spectrophotometric control was employed using several established compounds as references. The presence of ethylenic bonds was confirmed by reduction with Adam's catalyst (PtO_2) in ethyl acetate of artobiloxanthone (**3a**) to give the tetrahydro derivative. Reduction of the trimethyl ether (**3b**) with Pd–$CaCO_3$ in methanol did not

*Author to whom correspondence should be addressed at: Department of Organic Chemistry, Queen's University of Belfast, Belfast BT9 5AG, U.K.



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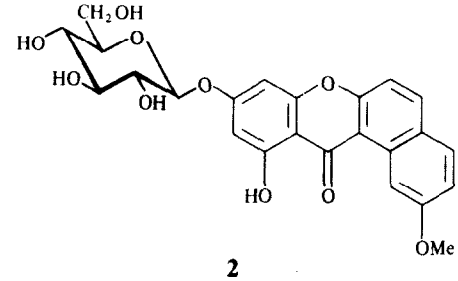

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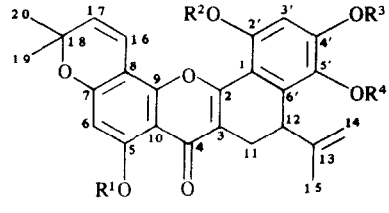
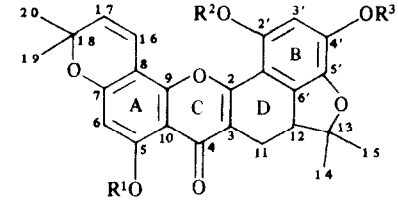




3a $R^1 = R^2 = R^3 = R^4 = H$
3b $R^1 = H$, $R^2 = R^3 = R^4 = Me$
3c $R^1 = R^2 = R^3 = R^4 = Ac$

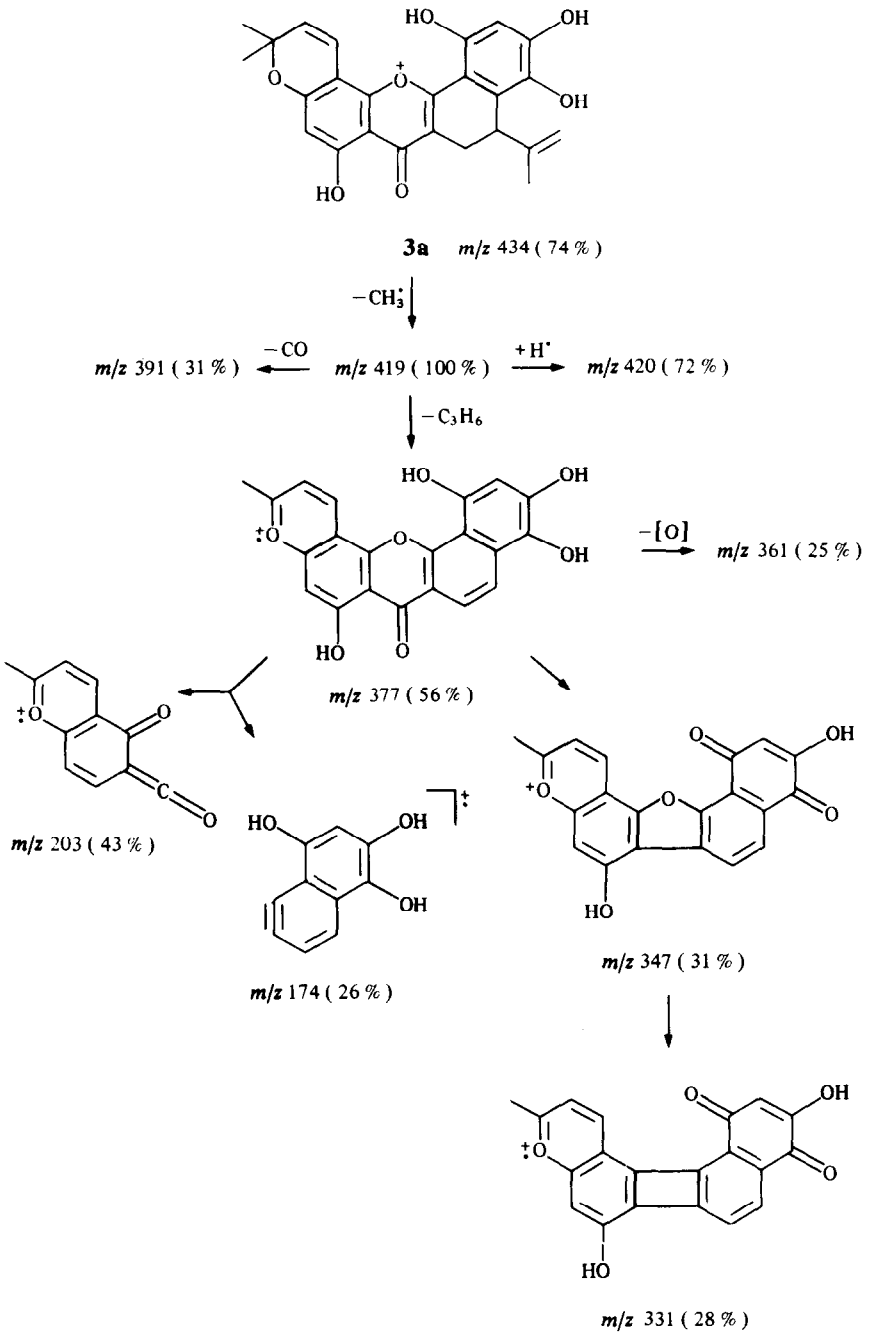
4a $R^1 = R^2 = R^3 = H$
4b $R^1 = H$, $R^2 = R^3 = Me$
4c $R^1 = R^2 = R^3 = Ac$

affect the propenyl double bond and gave a dihydro derivative of **3b**. The orientation of the substituents as shown in **3a** can be deduced as follows. The presence of two singlets for the two aromatic protons suggests that they are present in an isolated environment. Assignment of the chelated hydroxy group at C-5 and the presence of an angular chromen ring indicate that the other three hydroxyl groups in **3a** are attributed to the B-ring. Two adjacent hydroxy groups are ascribed to the 4′ and 5′ position and the third hydroxy group becomes *para* to 5′ and assigned to the 2′-position, in accordance with the negative Gibb's test [11].

The mass spectra [13] of artobiloxanthone, its trimethyl ether and hydrogenated product were consistent with the assigned structure (see Scheme 1). The foregoing evidence, together with the ^{13}C NMR data (Table 1) [14–17] indicate structure **3a** for artobiloxanthone.

The least polar yellow pigment, mp 285–287°, $[M]^+$ *m/z* 434.1366 (high resolution) has the molecular formula, $C_{25}H_{22}O_7$. It was also as isomeric diprenylated pentaoxygenated dihydroxanthone and was named cycloartobiloxanthone (**4a**). It gave a dimethyl ether (**4b**) with diazomethane and a triacetate (**4c**) indicating the presence of three phenolic groups, one of which is chelated (δ13.33) to a carbonyl group. The IR spectrum showed a hydroxy band (3400 cm^{-1}) and conjugated carbonyl frequency (1650 cm^{-1}).

The ^1H NMR spectrum was similar to that of artobiloxanthone (**3a**) but, with the absence of isopropenyl group signals. The olefinic doublets at δ6.92 and 5.64 (J = 10 Hz) in acetone-d_6, the superimposed two methyl groups at δ1.47 (6H) together with the base peak at *m/z* 419 $[M-15]^+$ in the mass spectrum confirmed the presence of the 2,2-dimethylchromene ring [6]. The angular orientation of the chromene ring was confirmed by the induced paramagnetic shifts [10] as before (Table 2) and negative Gibb's test [11]. The aromatic protons appeared as singlets at δ6.43 and 6.14 and the latter was assigned to H-6 as in artobiloxanthone (**3a**) and 6-deoxyisojacareubin (**6**) [8] which also showed an upfield shift in aromatic signals. The UV spectrum showed absorptions at λ_{max}^{MeOH} (log ε) 235 (4.37), 282 (4.46), 333 sh (4.02) and 394 (4.18) nm and the high intensity absorption in the long wave length region (Band I) was attributed to the maximum conjugation of the B-ring with the chromone ring. This must be due to the co-planarity of these two rings as in cycloartocarpin (**7**) [2] and neohydnocarpin (**5**) [7]. In contrast to artobiloxanthone, the UV spectrum of cycloartobiloxanthone (**4a**) does not undergo a bathochromic shift in the presence of $NaOAc-H_3BO_3$ showing that, the hydroxyls are not *ortho* to each other [5]. The appearance of two singlets at δ1.67 and 1.34 (3H each) in the ^1H NMR spectrum in addition to the ABX type of signals as before at δ2.36 (*t*), 3.21 (*dd*) and 3.43 (*dd*) can be



Scheme 1.

explained as due to the dihydrofuran ring, which could arise from artobiloxanthone (**3a**) by the oxidative cyclization of the 5′-hydroxy group of the B-ring onto the isoprenyl side chain. This structure was confirmed by the formic acid cyclization of artobiloxanthone (**3a**) to yield cycloartobiloxanthone (**4a**) (16%).

Furthermore, dehydrogenation of cycloartobiloxanthone dimethyl ether (**4b**) with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in benzene, yielded pyranobenzoxanthone (**8b**). The ^{1}H NMR spectrum of **8b** clearly revealed the appearance of a striking down field aromatic singlet at δ7.74, in addition to the aromatic singlets at δ6.73, 6.30 and the downfield signal (δ13.10) for the chelated hydroxy group. The downfield singlet at δ7.74 must be due to the newly formed aromatic proton at H-11 which is *peri* to the carbonyl group; the signals at δ 6.73 and 6.30 are assigned to H-3′ and H-6, respectively. The UV spectrum of the pyranoxanthone (**8b**) exhibited a bathochromic shift ($\Delta\lambda$ 32 nm) in Band I, relative to that of the parent cycloartobiloxanthone dimethyl ether (**4b**),

Table 1. Assignments of ^{13}C NMR signals of **1**, **3a** and **4a** (in acetone-d_6)

C	1	3a	4a
2/7	161.4 *s*	162.5 *s*	162.8 *s*
3	104.3 *d*[a]	102.0 *s*	102.1 *s*
4	182.4 *s*	181.8 *s*	181.9 *s*
5	152.2 *s*	152.6 *s*	152.4 *s*
6	100.7 *s*	101.1 *d*	102.2 *d*
7/2	162.2 *s*	163.1 *s*	163.1 *s*
8	99.1 *d*	107.3 *s*	105.2 *s*
9	158.9 *s*	159.9 *s*	158.6 *s*
10	104.6 *s*[a]	105.7 s	105.2 s
11	23.8 *t*	22.3 *t*	20.5 *t*
12	121.9 *d*	38.2 *d*	47.7 *d*
13	131.7 *s*	137.1 *s*	93.9 *s*
14	17.4 *q*[b]	112.2 *t*	22.9 *q*[a]
15	25.5 *q*[b]	22.0 *q*	29.1 *q*[a]
16	114.6 *d*	116.4 *d*	116.3 *d*
17	127.9 *d*	128.4 *d*	128.2 *d*
18	78.2 *s*	78.8 *s*	78.9 *s*
19	27.8 *q*	28.3 *q*	28.3 *q*
20	27.8 *q*	28.3 *q*	28.3 *q*
1′	120.3 *s*	118.3 *s*	113.0 *s*
2′	149.2 *s*[c]	152.0 *s*[a]	151.9 *s*
3′	109.8 s	104.0 *d*	106.8 *d*
4′	149.0 *s*[c]	151.4 *s*[a]	147.8 *s*
5′	138.5 *s*	145.7 *s*	138.6 *s*
6′	1165 *d*	130.3 *s*	134.0 *s*

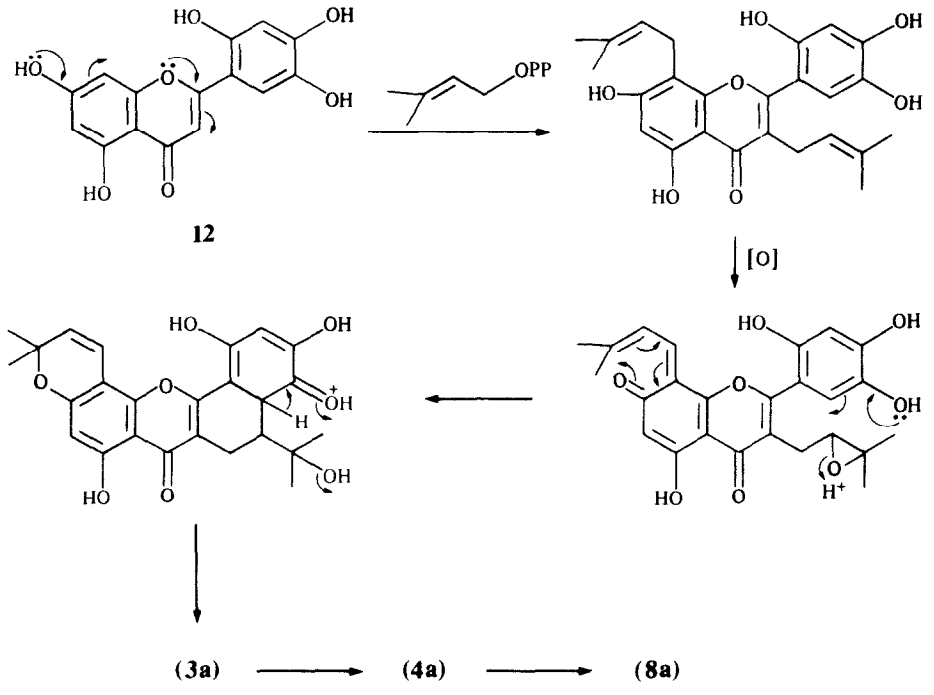
[a–c] Values may be interchanged. (*s*-singlet, *d*-doublet, *t*-triplet and *q*-quartet refer to the appearance of the resonance in the single frequency off-resonance mode experiments).

Table 2. Chemical shift differences (in $CDCl_3$).

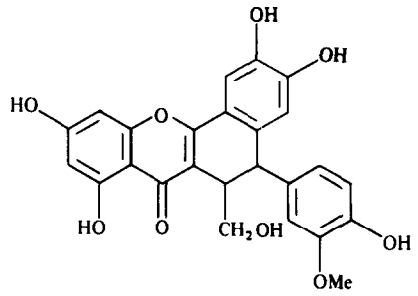
	H-16	H-17	H-6	H-3′
Methyl ether (**3b**)	6.85	5.55	6.23	6.54
Acetate (**3c**)	6.92	5.72	6.50	7.13
para-magnetic shift ($\Delta\delta$)	−0.07	−0.17	−0.27	−0.59
Methyl ether (**4b**)	6.85	5.58	6.26	6.40
Acetate (**4c**)	6.85	5.72	6.50	6.74
para-magnetic shift ($\Delta\delta$)	−0.00	−0.14	−0.24	−0.34

indicating the extended conjugation in the molecule. The ^{13}C NMR spectrum [14–17] is consistent with the proposed structure for cycloartobiloxanthone (**4a**) (Table 1).

An alternative proposal for artobiloxanthone and cycloartobiloxanthone as **9** and **10**, respectively, can be ruled out as follows. The chemical shifts of the ABX system of signals in the ^1H NMR spectrum of **3a** and **4a** has the X-type proton, which was simultaneously allylic and benzylic shifted from δ3.94 in **3a** to 3.21 in **4a** whilst the A,B type protons showed the expected correspondence in **3a** and **4a** (see Experimental). Structures **9** and **10** cannot have A,B type protons ($H_{\alpha\beta}$-12) unaffected when the isopropenyl side chain cyclises with the hydroxy group to give the chroman ring in **10**. Additionally, the mass spectral fragmentations [6, 18] are also in favour of a xanthonoid skeleton in **3a** and **4a** (see Scheme 1 for **3a**) The pyranobenzoxanthone arising from an isoflavonoid chromophore to give **11** can also be dismissed by considering both the UV spectral data and the down field aromatic proton signal at δ7.74. This type of down field shift due to the deshielding effect of the carbonyl group has been extensively used in the assignment of xanthones [19–21].



Scheme 2.



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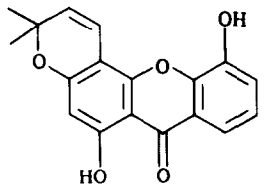

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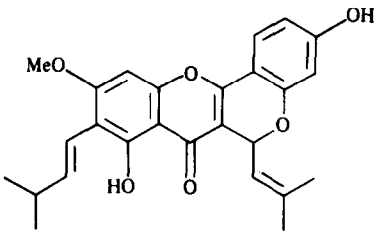

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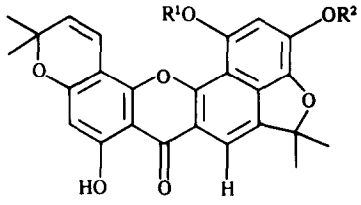
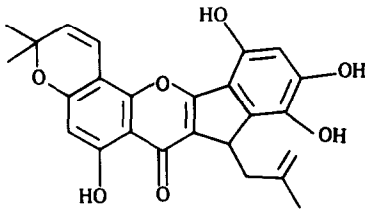


8a $R^1 = R^2 = H$
8b $R^1 = R^2 = Me$



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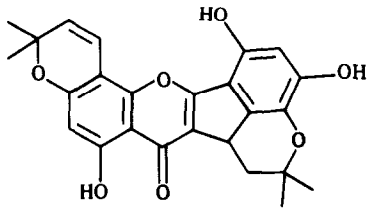

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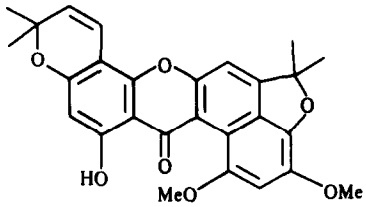

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A feasible biosynthetic route for the formation of artobiloxanthone (**3a**) and cycloartobiloxanthone (**4a**) from a simple flavone (**12**) is suggested in Scheme 2. The epoxidation–dehydration mechanism is similar to that proposed for the biosynthesis of the rotenoid, amorphigenin [22]. As artobiloxanthone (**3a**) and artobilochromen (**1**) have the same oxygenation pattern as the simple flavone (**12**), a biogenetic relationship between dihydrobenzoxanthones and flavones seems likely.

EXPERIMENTAL

Bark of *A. nobilis* Thw. was collected in the Kanneliya rain forest in the South of Sri Lanka. The bark was chipped, air-dried and powdered in a mill. Sequential extraction of the powdered bark (4.5 kg) was carried out using hot petrol, hot C_6H_6 and hot MeOH. Weights of the extracts obtained were, petrol (48 g, 1.1%), C_6H_6 (98 g, 2.10%) and MeOH (150 g, 3.29%). The C_6H_6 extracts (10 g) was triturated with $CHCl_3$, filtered and the filtrate extracted with MeOH–H_2O (1:9). Addition of *n*-hexane to the $CHCl_3$ soluble portion pptd a yellow solid (2.16 g, 0.46%). This was subjected to CC over silica gel, eluting with Me_2CO–C_6H_6 mixts.

Cycloartobiloxanthone (**4a**). Elution with Me_2CO–C_6H_6 (1:9) yielded an orange semi-solid which was dissolved in C_6H_6. Addition of petrol pptd a yellow solid. This on further purification by prep. TLC in Me_2CO–C_6H_6 (1:2) gave cycloartobiloxanthone (**4a**) as a dark yellow solid, mp 285–287° (from

MeOH), (140 mg, 3.01×10^{-2}%) (Found: $[M]^+$ *m/z* 434.1366 ($C_{25}H_{22}O_7$), $C_{25}H_{22}O_7$ requires 434.4441); UV λ_{max}^{MeOH} nm (log ε): 235 (4.37), 282 (4.46), 333 sh (4.02) and 394 (4.18). $\lambda_{max}^{MeOH+AlCl_3}$ nm (log ε): 239 (4.46), 294 (4.49), 325 (4.42), 357 (4.34) and 436 (4.41). $\lambda_{max}^{MeOH+NaOAc}$ nm (log ε): 237 (4.35), 282 (4.46) and 406 (4.17). No shift was observed with NaOAc–H_3BO_3. IR ν_{max}^{KBr} cm^{-1}: 3400, 3200 (OH) and 1650 (C=O). ^1H NMR (200 MHz, acetone-d_6): δ13.33 (1H, *s*, chelated OH), 8.85 (OH), 8.70 (OH), 6.92 (1H, *d*, H-16, *J* = 10 Hz), 6.43 (1H, *s*, H-3′), 6.14 (1H, *s*, H-6), 5.64 (1H, *d*, H-17, *J* = 10 Hz) 3.43 (1H, *dd*, *J* = 7 and 14 Hz, H-11), 3.21 (1H, *dd*, *J* = 7 and 14.5 Hz, H-12), 2.36 (1H, *t*, *J* = 14.5 Hz, H-11), 1.67 (3H, *s*, Me), 1.47 (6H, *s*, 2 × Me), 1.34 (3H, *s* Me). MS *m/z* (rel. int) 434 ($[M]^+$, 74%), 420 (77), 419 (100), 417 (51), 391 (55), 377 (52), 363 (32), 361 (29), 347 (35), 337 (32), 293 (35), 203 (49) and 201 (40). For ^{13}C NMR (acetone-d_6) see Table 1. Cycloartobiloxanthone (50 mg) with CH_2N_2–Et_2O, gave cycloartobiloxanthone di Me ether (**4b**) as dark yellow needles (44 mg, 83%), mp 254° (from MeOH). $[M]^+$, *m/z* 462.1678 ($C_{27}H_{26}O_7$), $C_{27}H_{26}O_7$ requires 462.1678). UV $\lambda_{max}^{MeOH-CHCl_3\ 7:3}$ nm (log ε): 258 sh (4.18), 287 (4.30) and 394 (4.04). IR ν_{max}^{KBr} cm^{-1}: 2910, 2830 (OMe), 1630 (C=O) and 1560. ^1H NMR (60 MHz, $CDCl_3$): δ13.03 (1H, *s*, chelated OH), 6.85 (1H, *d*, H-16, *J* = 10 Hz), 6.40 (1H, *s*, H-3′), 6.26 (1H, *s* H-6), 5.58 (1H, *d*, H-17, *J* = 10 Hz), 3.96 (3H, *s*, OMe), 3.93 (3H, *s*, OMe), 3.40 (1H, *m*, H-11), 3.23 (1H, *m*, H-12), 2.26 (1H, *t*, *J* = 12 Hz, H-11), 1.63 (3H, *s*, Me), 1.43 (6H, *s*, 2 × Me), 1.26 (3H, *s*, Me). Cycloartobiloxanthone (64 mg) with Ac_2O (1 ml) and pyridine (3 ml) gave a mixt which on sepn by prep. TLC gave a diacetate as pale yellow needles, mp 284° (MeOH). $[M]^+$ *m/z* 518.1570 ($C_{29}H_{26}O_9$), $C_{29}H_{26}O_9$ requires 518.1576) and a triacetate (**4c**) as off-white needles. mp 279–281° (MeOH–$CHCl_3$). $[M]^+$ *m/z* 560.1646 ($C_{31}H_{28}O_{10}$) $C_{31}H_{28}O_{10}$ requires 560.1682). IR ν_{max}^{KBr} cm^{-1}: 1760 (C=O). ^1H NMR (60 MHz, $CDCl_3$): δ6.85 (1H, *d*, H-16, *J* = 10 Hz), 6.74 (1H, *s*, H-3′), 6.50 (1H, *s*, H-6), 5.72 (1H, *d*, H-17, *J* = 10 Hz), 3.36–2.40 (*m*, 3H), 2.45 (3H, *s*, OAc), 2.33 (6H, *s*, 2 × OAc), 1.68 (3H, *s* Me), 1.54 (3H, *s*, Me), 1.50 (3H, *s* Me), 1.40 (3H, *s*, Me).

Artobilochromen (**1**). Artobilochromen was isolated by CC by elution with Me_2CO–C_6H_6 (1:4) and from the $CHCl_3$ insol portion of the C_6H_6 ext of the bark (289 mg, 6.03×10^{-2}%). This on purification by prep. TLC and recrystallization from $CHCl_3$–MeOH yielded bright yellow crystals, mp 246–248° (lit. [1], mp 244°) identical with a sample isolated previously [1].

Artobiloxanthone (**3a**). Further elution with Me_2CO–C_6H_6 (1:4) afforded a yellow solid containing mainly artobiloxanthone and artobilochromen. These were initially purified by prep. TLC and the band containing artobiloxanthone was dissolved in C_6H_6. By repeated pptn with petrol, pure artobiloxanthone was obtained as a yellow solid, mp 162–164°. $[M]^+$ *m/z* 434.1307 ($C_{25}H_{22}O_7$), high resolution MS, $C_{25}H_{22}O_7$ requires 434.1306). UV $\lambda_{max}^{CHCl_3-MeOH\ 1:9}$ nm (log ε): 265 (4.34), 285 (4.35), 315 (sh) (4.07) and 394 (4.02). $\lambda_{max}^{MeOH-CHCl_3\ 9:1+AlCl_3}$ nm (log ε): 293 (4.29), 320 sh (3.99) and 460 (4.12). $\lambda_{max}^{MeOH-CHCl_3 9:1+NaOAC}$ nm (log ε) 267 (4.39), 328 (sh) (4.19) and 428 (3.83). $\lambda_{max}^{MeOH-CHCl_3\ 9:1+NaOAc+H_3BO_3}$ nm (log ε): 265 (4.37), 300 (4.29) and 328 (4.19). IR ν_{max}^{KBr} cm^{-1}: 3300 (OH) and 1650 (C=O). ^1H NMR (200 MHz, $CDCl_3$), δ13.30 (1H, *s*, chelated OH), 6.92 (1H, *d*, H-16, *J* = 10 Hz), 6.57 (1H, *s*, H-3′), 6.10 (1H, *s*, H-6), 5.64 (1H, *d*, H-17, *J* = 10 Hz), 4.60 (1H, *m*, CH_2 =, H-14), 4.30 (1H, *m*, CH_2=, H-14), 3.94 (1H, *d*, *J* = 8 Hz, H-12), 3.42 (1H, *dd*, *J* = 2 and 16 Hz, H-11), 2.37 (1H, *dd*, *J* = 8 and 16 Hz, H-11), 1.74 (3H, *s*, Me–C =), 1.40 (6H, *s*, 2 × Me). MS *m/z* (rel. int): ($[M]^+$, 74%), 420 (72), 419 (100), 393 (31), 391 (31), 377 (56), 361 (25), 347 (31), 331 (28), 217 (21), 203 (43), 174 (26), 166 (34). For ^{13}C NMR, see Table 1. The tri Me ether (CH_2N_2) afforded bright yellow needles (42 mg, 76%), mp 248° (MeOH). $[M]^+$ *m/z* 476.1837 ($C_{28}H_{28}O_7$), $C_{28}H_{28}O_7$ requires 476.1834). UV λ_{max}^{EtOH} nm (log ε): 248 sh (3.96), 273 sh (3.83), 283 (3.84), 307 (3.49), 348 sh (3.55) and 376 (3.58). IR ν_{max}^{KBr} cm^{-1}: 1640 (C=O). ^1H NMR (60 MHz, $CDCl_3$): δ13.12 (1H, *s*, chelated OH), 6.85 (1H, *d*, H-16, *J* = 10 Hz), 6.54 (1H, *s*, H-3′), 6.23 (1H, *s*, H-6), 5.55 (1H, *d*, H-17, *J* = 10 Hz), 4.73 (1H, *m*, CH_2 =, H-14), 4.23 (1H, *m*, CH_2 =, H-14), 3.97 (6H, *s*, 2 × OMe), 3.77 (3H, *s*, OMe), 3.57 (1H, *m*, H-12), 3.36 (1H, *m*, H-11), 2.40 (1H, *dd*, *J* = 8 and 16 Hz, H-12), 1.83 (3H, *s*, Me–C =), 1.50 (3H, *s*, Me), 1.45 (3H, *s*, Me). Artobiloxanthone (30 mg) with Ac_2O (1 ml) and pyridine (3 ml) yielded the tetraacetate of artobiloxanthone as a semi-solid (**3c**) (34 mg, 83%). It gave no colouration with iron (III) chloride. ($[M]^+$ *m/z* 602. 1813 ($C_{33}H_{30}O_{11}$), $C_{33}H_{30}O_{11}$ requires 602.1787). ^1H NMR (60 MHz, $CDCl_3$) δ7.13 (1H, *s*, H-3′), 6.92 (1H, *d*, *J* = 10 Hz, H-16), 6.50 (1H, *s*, H-6), 5.72 (1H, *d*, *J* = 10 Hz, H-17), 4.73 (1H, *m*, CH_2=, H-14), 4.33 (1H, *m*, CH_2=, H-14), 3.77 (1H, *br m*, H-12), 3.30 (1H, *m*, H-11), 2.83 (1H, *dd*, *J* = 8 and 16 Hz, H-11), 2.43 (3H, *s*, OAc), 2.30 (9H, *s*, 3 × OAc), 1.73 (3H, *s*, Me-C =), 1.53 (3H, *s*, Me), 1.50 (3H, *s*, Me).

Dihydroartobiloxanthone trimethylether. Arotobiloxanthone tri Me ether (**3b**) (34 mg) in $CHCl_3$–MeOH was hydrogenated for 24 hr with Pd–$CaCO_3$ (40 mg) as catalyst. The hydrogenated product was purified by prep. TLC and recrystallized from MeOH to give a yellow crystalline solid, mp 216–218°, $[M]^+$, *m/z* 478.1933 ($C_{28}H_{30}O_7$), $C_{28}H_{30}O_7$ requires 478.1932); IR ν_{max}^{KBr} cm^{-1}: 1640 (C=O). ^1H NMR (60 MHz, $CDCl_3$) δ12.70 (1H, *s*, chelated OH), 6.53 (1H, *s*, H-3′), 6.20 (1H, *s*, H-6), 4.70 (1H, *m*, CH_2=, H-14), 4.23 (1H, *m*, CH_2=, H-14), 3.97 (6H, *s*, 2 × OMe), 3.77 (3H, *s*, OMe), 3.60 (1H, *m*, H-12), 3.30 (1H, *m*, H-11), 2.87 (1H, *m*, H-11), 2.10–2.67 (4H, *m*, H-16,17), 1.80 (3H, *s*, Me–C =), 1.37 (6H, *s*, 2 × Me). MS *m/z* (rel. int): 478 ($[M]^+$, 100%), 463 (81), 437 (90), 423 (60), 407 (41), 381 (61), 351 (53), 279 (36), 239 (42), and 221 (35). Under these conditions the isopropenyl double bond was not reduced.

Tetrahydroartobiloxanthone. Artobiloxanthone (40 mg) in EtOAc (20 ml) was hydrogenated over Adam's catalyst (PtO_2) (30 mg) for 3 hr. Catalyst was filtered off and the reaction mixt concd. On purification by prep. TLC, it gave tetrahydroartobiloxanthone as a semi-solid. ^1H NMR (60 MHz, acetone-d_6): δ13.00 (1H, *s*, chelated OH), 8.20 (*br*, OH), 6.53 (1H, *s*, H-3′), 6.13 (1H, *s*, H-6), 2.0–3.60 (8H, *m*), 0.97 (3H, *s*, Me), 0.96 (3H, *s*, Me), 0.83 (6H, *d*, 2 × Me).

Cyclization of artobiloxanthone. Artobiloxanthone (42 mg) was warmed with HCO_2H (10 ml) for 30 min. Ice-cold H_2O was added and the yellow solid obtained filtered off, washed well with cold 5% $NaHCO_3$ soln and H_2O. Purification by prep. TLC gave a yellow solid (7 mg, 16%), identified as cycloartobiloxanthone by comparison with an authentic sample (mp, mmp, UV, IR and co-TLC.

Pyranobenzoxanthone dimethyl ether (**8b**). Cycloartobiloxanthone di Me ether (15.0 mg) was refluxed with DDQ (10.0 mg) in C_6H_6 (10 ml) for 16 hr. After solvent evapn the benzoxanthone was sepd by prep. TLC ($CHCl_3$) and isolated as yellow needles, mp 274° (MeOH), (8 mg, 57%), $[M]^+$ *m/z* 460.1523 ($C_{27}H_{24}O_7$), $C_{27}H_{24}O_7$ requires 460.1522). UV $\lambda_{max}^{MeOH-CHCl_3\ 7:3}$ nm (log ε): 273 (4.37), 305 (4.47) and 426 (4.14). $\lambda_{max}^{MeOH-CHCl_3\ 7:3+AlCl_3}$ nm (log ε): 280 (4.35), 324 (4.47) and 484 (4.25). IR ν_{max}^{KBr} cm^{-1} 3440 (OH), 2920 (OMe), 1655, 1630. ^1H NMR (200 MHz, $CDCl_3$): δ13.10 (1H, *s*, chelated OH), 7.74 (1H, *s*, H-11), 7.02 (1H, *d*, H-16, J = 10 Hz), 6.73 (1H, *s*, H-3′), 6.30 (1H, *s*, H-6), 5.64 (1H, *d*, H-17, *J* = 10 Hz), 4.14 (3H, *s*, OMe), 4.08 (3H, *s*, OMe), 1.77 (6H, *s*, 2 × Me), 1.53 (6H, *s*, 2 × Me). MS *m/z* (rel. int): 460 ($[M]^+$, 60), 445 (100), 430 (13), 415 (14) and 215 (22).

Acknowledgements—We thank Prof. R. H. Thomson (University of Aberdeen) for useful discussions and some spectral data, Dr. P. Bladon (University of Strathclyde) for ^{13}C NMR data, Prof. S.

Balasubramaniam (Department of Botany) for the identification of plant species and the University of Peradeniya, Sri Lanka, for financial assistance.

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